

Benzene removal over a fixed bed of wood char: The effect of pyrolysis temperature and activation with CO₂ on the char reactivity

Luisa Burhenne^{*}, Thomas Aicher

Fraunhofer-Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany

ARTICLE INFO

Article history:

Received 19 February 2014

Received in revised form 12 May 2014

Accepted 19 May 2014

Available online 7 July 2014

Keywords:

Benzene
Biomass
Char reactivity
Fixed bed gasification
Pyrolysis
Wood char structure

ABSTRACT

Benzene removal using spruce wood char as catalyst was investigated. The influence of pyrolysis temperature and activation with CO₂ on the char structure and reactivity for benzene adsorption and cracking was analyzed. The structural features of the char were examined by the CO₂ adsorption technique and Fourier transform infrared spectroscopy (FTIR). The reactivity for benzene removal was investigated using a fixed bed quartz reactor. Surface analysis showed that the microporous char surface area was influenced by the pyrolysis temperature and was almost doubled by activation with CO₂.

The benzene adsorption capacity of the char decreased with increasing pyrolysis temperature. Activation with CO₂ however, increased the fraction of adsorbed benzene by a factor of two and 10 for char produced at 500 and 800 °C, respectively. The total microporous surface above 700 m²/g was found to be a good indicator for the reactive char surface for benzene cracking at high temperatures. At 1050 °C the main mode of benzene conversion was homogeneous thermal decomposition.

We confirmed that wood char has the potential to serve as an effective catalyst for benzene removal. However, benzene decomposed over the charcoal by carbon deposition which led to a fast deactivation of the wood char catalyst.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Biomass gasification is identified as one of the most promising renewable and CO₂ neutral technologies for the conversion of biomass into an energy containing product gas or fuel. In the case of fixed bed gasification, this product gas is mainly composed of permanent gases, i.e. CO, H₂, CO₂, CH₄, and N₂, in addition to unwanted organic condensable fractions that range from lower to higher hydrocarbons and differ strongly in size, decomposition and adsorption behavior [1,2]. In a meeting on the tar measurement protocol, held by the EU/IEA/US-DOE in Brussels in the year 1998, it was agreed by a number of experts to define all organic compounds with a molecular weight larger than benzene as “tar” [1–3]. However, benzene is still an unwanted gasification product due to its carcinogenicity and its negative environmental impact. Reducing tar and benzene emissions remains one of the main challenges in the commercialization of small scale fixed bed gasifiers. Tars can be removed by thermal, catalytic or physical processes either within the gasification process (primary methods) or after the process (secondary methods). Primary methods, e.g. thermal and catalytic cracking, have the advantage that expensive gas cleaning systems can be avoided, while maintaining the sensible heat in the produced gas [4]. Carbon containing materials such as activated carbon or wood char were found by several researchers [5–7] to show a good catalytic

activity for tar removal by adsorption or cracking. Wood chars were found in several studies to be more reactive than coal chars, mainly because wood char has a less ordered structure and a high content of oxygen [8,9]. However, only very few studies have been conducted to investigate the impact of pyrolysis conditions on the char reactivity for catalytic tar removal [7,10,11].

In a review about charcoal production and properties, Antal and Groenli [12] summarize that the pyrolysis temperature has a strong impact on the surface area, pore structure, and adsorption properties of the charcoal. The structural evolution during pyrolysis of coal char at different temperatures and heating rates was investigated by Lu et al. [13] using the quantitative XRD analysis. M. Asadullah et al. [14] conducted comparable investigations with mallee wood chars using Raman spectroscopy. Both found that with increasing pyrolysis temperature the char structure became more ordered, i.e. the amorphous concentration of the char decreased, and the aromaticity of all chars increased.

Removal of biomass-derived tar by thermal and catalytic treatment has been investigated in numerous previous studies [4,5,15–17]. Most studies however, focus on the decomposition of methane for the production of hydrogen. Only recently some researchers focused on cracking and adsorption of higher hydrocarbons on wood char [7,10,11].

T. Phuphuakrat et al. [6] investigated the adsorption performance of light condensable tar on three adsorbents (activated carbon, wood chip, and synthetic porous cordierite) at a temperature between 25 and 30 °C. The adsorption performances of wood chips for light

^{*} Corresponding author.

hydrocarbons were almost similar to those of activated carbon, except for naphthalene. The study showed that non-condensable tar is easily adsorbed by micropore adsorbent materials such as activated carbon, while condensable tars are better adsorbed by mesopore material such as wood chips.

Moliner et al. [18] studied the effect of carbon structure on methane decomposition over different activated carbons. They found that only the initial reaction rate depends on the surface chemistry of the sorbent but that the long-term behavior is related to the char surface area and pore size distribution [9]. Hosokai et al. [19] confirmed their findings and demonstrated that benzene underwent decomposition mainly by coking in the micropores, causing loss of microporous surface area and then activity of the charcoal.

In view of the above-mentioned studies, it is expected that the surface of carbonized solid material would be capable to decompose tar to a significant conversion level [19] and that the surface area and chemistry are influencing parameters on the char capability for the adsorption and decomposition of light hydrocarbons, e.g. benzene [20].

However, in none of these studies decomposition of light aromatic compounds, e.g. benzene, was investigated into detail and the results were not correlated to different carbon structures. Hosokai et al. [19] state that the main mechanism of decomposition of aromatics over charcoal has not yet been understood. Still efforts have to be made to better understand the mechanisms of the reactions taking place on the char surface, both during adsorption and during decomposition to optimize the properties of the wood char particles and by adjusting the pyrolysis conditions [18]. So far the literature does not provide an understandable relationship between the pyrolysis temperature, the char structure and its reactivity for benzene removal.

The aim of this study was firstly to elucidate the effect of the pyrolysis temperature and CO₂ activation on the structure and the surface area of spruce wood char catalyst, and secondly to examine the impact of structural differences with respect to the char reactivity for benzene removal.

2. Materials and methods

2.1. Char sample preparation

2.1.1. Pyrolysis

Different kinds of wood char catalyst were produced by pyrolyzing dry spruce wood chips (*Picea abies* (L.) Karst. without bark) with a particle size between 10 mm and 20 mm, at both 500 °C and 800 °C and a heating rate of 30 °C/min. The main parameters adopted for pyrolysis are summarized in Table 1. Pyrolysis was performed in a vertical batch reactor. Details on the raw biomass materials and on the pyrolysis procedure have been reported elsewhere [9].

The char samples were crushed after pyrolysis and sieved so that a char catalyst with a particle size between 0.5 mm and 2.5 mm was obtained.

2.1.2. Activation in CO₂

A part of the pyrolysis char was activated with CO₂ in a vertical tubular quartz reactor with a length of 110 mm and an internal diameter of 18 mm heated by an electrical furnace (Fig. 1). The main parameters adopted for activation are summarized in Table 1.

10 g of sample mass was placed inside the quartz reactor supported by a quartz wool layer. The temperature of the sample was monitored and controlled by a thermocouple located inside the bed of char and connected online to a Lab-View system design platform [9]. The char sample was heated from room temperature to 800 °C under a continuous nitrogen flow. When the final temperature was reached, 0.166 l/min of CO₂ (45% of the total flow) and 0.2 l/min of nitrogen were mixed and then purged into the quartz reactor for 1.5 h. The CO₂ and N₂ were fed from a 25 kg compressed gas cylinder and the building's

Table 1

Main experimental parameters adopted during pyrolysis, char activation in CO₂, benzene adsorption and benzene decomposition.

Parameter	Pyrolysis	CO ₂ activation	Benzene adsorption	Benzene decomposition
Sample mass (g)	30	10	6	6
Nitrogen volume percentage (%)	100	55	99.9	99.9
CO ₂ volume percentage (%)	0	45	0	0
Benzene volume percentage (%)	0	0	0.13	0.13
Benzene concentration (g/m ³)	0	0	4.5	4.5
Gas flow rate (l/min)	1	0.4	3.2	1.6
Gas residence time (s)		5.5	0.6	0.8
Gas velocity in reactor (cm/s)		2.4	21	10.5
Final temperature (°C)	500, 800	800	27	850, 950, 1050

gas supply, respectively, and the flow rates were controlled by two independent mass flow controllers. The gas velocity in the reactor was about 2.4 cm/s which corresponds to a residence time in the bed of 5.5 s.

The char samples produced at a pyrolysis temperature of 500 °C were exposed to flowing CO₂ already at 500 °C and heated to 800 °C at a constant heating rate of 10 °C/min. The total time of activation was always 1.5 h (0.5 h for the heating up and 1 h at a constant temperature of 800 °C). At the end of activation in CO₂, the char sample was cooled down to room temperature under a continuous flow of nitrogen (1–2 l/min).

In total, four types of spruce wood char were generated and were named as follows: *P 500* and *P 800* which denote char produced by pyrolysis at 500 and 800 °C, respectively and *P 500 act.* and *P 800 act.* which denote their activated versions.

2.1.3. Commercial activated carbon

All experiments were repeated with a standard material in order to compare the results. Therefore, commercial activated carbon (DFG 2 super), kindly provided by CarboTech AC GmbH, was used. The activated carbon was provided in pellet shape with a diameter of 2 mm and a bulk density of 430 ± 30 g/l. The BET surface is given by the supplier as 1100 m²/g, analyzed with N₂ adsorption technique, and the pore volume was given as 0.92 cm³/g, analyzed using Hg porosimetry.

2.2. Char characterization

2.2.1. Surface area and pore size

The total surface area of each char sample was measured through nitrogen and CO₂ adsorption at −196 and 0 °C, respectively. Prior to measurements, the sample was outgassed for 12 h at 250 °C. The amount of nitrogen or CO₂ adsorbed at a relative pressure of $p/p_0 = 0.98$ or $p/p_0 = 0.03$, respectively, was used to evaluate the total pore volume (V_T) or the microporous volume (V_{mp}), respectively. The pore volume and the pore size distribution in the range of 8–2500 Å and 4–10 Å for nitrogen or CO₂, respectively, were determined by applying the density functional theory (DFT). Feng and Bhatia [20] state that there are two widely used classical methods to determine the pore surface area of carbon by physical gas adsorption. One is the Brunauer–Emmett–Teller (BET) theory, most commonly employed with the nitrogen isotherm. The other is the Dubinin–Radushkevich (DR) equation, most often used to determine a CO₂ adsorption isotherm.

Nitrogen is known to be subject to very slow diffusion in small pores [20], whereas CO₂ cannot fill larger pores. In this study, nitrogen adsorption measurements showed very low reproducibility and very high standard deviations, whereas the results obtained by CO₂ adsorption were comparable to available literature [21–23]. Sanchez et al. [21] advised to establish differences between wide and narrow microporosity by different adsorptives such as CO₂, which appears to measure a

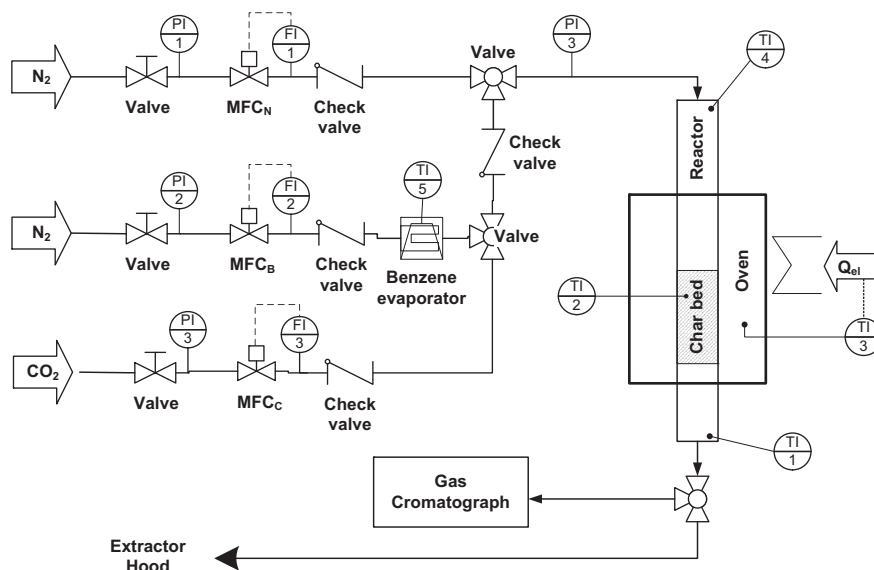


Fig. 1. Experimental set-up used for activation of the wood char samples in CO_2 , for benzene adsorption and benzene cracking experiments (N_2 = nitrogen; CO_2 = carbon dioxide; PI = pressure indicator; FI = flow indicator; TI = temperature indicator; MFC = mass flow controller).

narrower porosity range than nitrogen. The amount of narrow or wider micropores depends mostly on the biomass precursor [21,24]. Most probably the spruce char samples produced in this study consisted mainly of narrow micropores with a diameter of about 5 Å. This diameter is known to be critical for nitrogen adsorption measurements due to blocking of the nitrogen molecules at the pore entrance. Therefore, only the microporous surface area and pore volume, determined from CO_2 adsorption isotherms using DR equation and density functional theory, were used in this study.

All surface measurements were carried out by courtesy of the department *Thermal Systems and Buildings* of the Fraunhofer ISE with the Quantachrome BET analyzer. Two replicates for each char sample, i.e. *P 500*, *P 800*, *P 500 act.*, and *P 800 act.* were analyzed.

2.2.2. Surface chemistry

Further surface analysis was performed using Fourier transform infrared spectroscopy (FTIR). FTIR absorbance spectra were recorded on a Perkin Elmer FTIR spectrometer (Spectrum 65). The samples were mixed with KBr (Merck; Uvasol; FTIR grade), homogenized in a mortar and 13 mm KBr pellets were prepared under vacuum in a standard device under a pressure of 75 kN cm^{-2} for 3 min. Typically, 5–10 mg sample mass was used at a concentration of 1–2% in KBr. 32 scans per sample were collected in the wave number range of $4000\text{--}400 \text{ cm}^{-1}$ in absorption mode at a spectral resolution of 4 cm^{-1} , and the collected spectra were then individually examined.

The FTIR spectral peak assignments were interpreted based on characteristic vibrations for wood and biochars [25–27].

2.3. Benzene removal in a fixed bed

The parameters adopted in the benzene removal experiments are summarized in Table 1.

2.3.1. Benzene adsorption and desorption

Adsorption of benzene on the different char samples was investigated at room temperature ($23\text{--}27^\circ\text{C}$) in the same experimental set-up used for char activation (Fig. 1). In each adsorption trial, a 6 g char sample was placed in the quartz reactor. Benzene was provided in gas phase using a laboratory evaporator filled with liquid benzene and purged with nitrogen as carrier gas. In order to get a low amount of benzene in nitrogen, the benzene evaporator was cooled down

to -6°C through an external glycol chiller; at that temperature, the volume percentage of benzene in nitrogen is about 2.08%. The benzene was of reagent grade with a purity over 99% and used without further purification. The nitrogen flow going into the evaporator was 0.2 l/min and was controlled by a mass flow controller. The nitrogen/benzene mixture coming out from the evaporator was diluted with an additional 3 l/min of nitrogen controlled by a second mass flow controller. As a result, the volume percentage of benzene going into the reactor during adsorption was about 0.13%, corresponding to about 4.5 g of benzene per cubic meter of flow gas. The pressure in the reactor was monitored by a pressure indicator installed before the quartz reactor. The pressure in the system was 0.05 bar(g) in all experiments and was controlled manually through the valve at the outlet of the reactor. In case of pressures above 0.05 bar(g), more product gas was led to the extractor hood.

The gas coming out from the quartz reactor was analyzed in the gas chromatograph every 3 min. The amount of benzene adsorbed in the sample was computed as the difference between the benzene volume percentage without the sample $V_{b,in}$ (0.13 and 0.14%) and the recorded amount of benzene after the reactor $V_{b,out}$ (measured with the gas chromatograph).

Desorption was carried out after adsorption by purging 1 l/min nitrogen through the char sample while heating it up from room temperature to 400°C at a heating rate of 50°C/min . The amount of benzene coming out of the reactor was measured in the gas chromatograph every 3 min to assure complete benzene desorption. At the end of desorption, the sample was cooled down to room temperature under a continuous flow of nitrogen (1–2 l/min). Two more adsorption and desorption cycles were carried out for all char samples. Between the cycles, the char was kept in the reactor and was continuously purged with nitrogen at ambient temperature and pressure.

2.3.2. Benzene cracking

The reactivity of the pyrolysis char for benzene cracking was investigated in a fixed bed by leading benzene through a hot bed of char at 850°C , 950°C , and 1050°C , and analyzing the released gaseous products. Three grams char sample was placed in the quartz reactor and heated up under a continuous nitrogen flow (1 l/min) with a heating rate of $15\text{--}16^\circ\text{C/min}$. At the final temperature, 0.1 l/min of nitrogen was purged in the benzene evaporator and diluted with additional 1.5 l/min of nitrogen concentration before entering the quartz

reactor. The final volume flows were chosen in order to reach the final benzene volume percentage of 0.13% (Table 1). The product gas was analyzed with an HP-PLOT-Q-column installed in an Agilent 6890N (G1540N) gas chromatograph. It was assumed that the higher the conversion of benzene, the higher was the reactivity of the char for the cracking of light aromatic compounds. Each experiment was repeated at least three times.

2.4. Statistical analysis

The accuracy of the measurements and the significance of the results were assessed evaluating the sample standard deviation and performing an analysis of variance (ANOVA), respectively. Both methods are described in detail elsewhere [9].

3. Results and discussion

3.1. Char characterization

3.1.1. Char yield after pyrolysis and activation

Spruce wood chips were pyrolyzed at both, 500 and 800 °C. A part of each sample was further activated by leading CO₂ at 800 °C through the char. The char yield after pyrolysis Y_{char} and activation $Y_{\text{char,act}}$ is given in percentage of the original biomass sample or the char after pyrolysis, respectively, according to the following equations.

$$Y_{\text{char}}(\%) = \frac{m_{\text{char}}}{m_{\text{bm}}} * 100 \quad (1)$$

$$Y_{\text{char,act}}(\%) = \frac{m_{\text{char,act}}}{m_{\text{char}}} * 100 \quad (2)$$

where, m_{char} , m_{bm} and $m_{\text{char,act}}$ denote the char weight after pyrolysis, the initial weight of the biomass and the char weight after activation, respectively. Table 2 summarizes the average char yields after pyrolysis Y_{char} and activation $Y_{\text{char,act}}$. The dry wood chips produced 25.3% and 20.7% chars, at 500 and 800 °C, respectively. According to the one way analysis of variance (ANOVA), the char yield decreased significantly with increasing pyrolysis temperature (p value = $1.13\text{E} - 5$). The initial pyrolysis temperature also affected the char yield after activation (p value = 0.021). The P 500 char samples underwent a greater mass loss due to activation than the P 800 char samples. This was most probably because the P 500 char underwent further outgassing during activation. Mass loss results at both temperatures were in line with available literature [22,28].

3.1.2. Char composition

The elemental analysis of all char samples was carried out at Fraunhofer UMSICHT according to the standard DIN 51732. The weight percentage of O was found as the difference between the total and the sum of the weight percentages of C, H, N, and ash (Table 3).

Pyrolysis temperature slightly affected the elemental composition of wood char. The weight percentage of hydrogen and oxygen was lower in the char produced at 800 °C; with activation, the weight percentage of carbon increased in both chars. In contrary, the weight percentage of oxygen and hydrogen decreased with char activation.

Table 2

Average char yields after pyrolysis at 500 and 800 °C, and after activation of these chars by CO₂ at 800 °C including standard deviation.

Pyrolysis temperature	Y_{char}	$Y_{\text{char,act}}$
500 °C	25 ± 2%	64 ± 3%
800 °C	21 ± 2%	71 ± 6%

The results are in line with the values presented by other researchers [8,12,29].

3.1.3. Surface area and pore size

The microporous surface area, the DFT pore volume and average pore size were measured by CO₂ adsorption for the original wood, the pyrolysis char, the activated samples as well as for the commercial activated carbon.

The microporous surface area of the wood was significantly increased by pyrolysis (p value = 0.003) and activation (p value = 0.0006). In fact, while the microporous surface area V_{mp} of the original wood was in average 126 m²/g, V_{mp} of the char samples ranged between 474 m²/g and 870 m²/g (Fig. 2).

When the pyrolysis temperature increased from 500 to 800 °C, the microporous surface area increased from 474 m²/g to 633 m²/g and the pore volume increased from 0.14 to 0.19 m³/g (Fig. 3, left hand side). The average micropore radius increased only slightly (Fig. 3, right hand side), indicating that the increase of surface area was probably due to the formation of new micropores in the char. This result is in contrast to our previous study, where we found a significant drop in the char surface area by increasing the pyrolysis temperature from 500 to 800 °C [9]. In our previous study we pyrolyzed the wood at a lower heating rate (4 °C/min) than in this study (30 °C/min), which resulted in longer residence times of the char in the hot zone, in particular for the char produced at 800 °C. Most likely, a longer residence time at higher temperatures favored thermal annealing of the char, which is supposed to be the main reason for the occlusion of most micropores during pyrolysis at 800 °C [14]. Thermal annealing, due to long residence times at temperatures above 800 °C was also found by several other researchers to decrease char reactivity significantly [13,30]. In addition, in our previous study we analyzed the microporous surface area by N₂ adsorption. Another reason for the very low surface area found in our previous study could be the kinetic blocking of the N₂ molecules at the entrance of the pores. This difference in surface area of the same material due to a different adsorbent illustrates the need for complementary techniques that would allow a more precise description of microporosity, mainly for heterogeneous carbons [21].

Activation with CO₂ led to a significant increase of the microporous char surface area and pore volume (Figs. 2 and 3, left). This effect was more remarkable at the lower pyrolysis temperature (p value = 0.0041): in fact, for the 500 °C char the microporous surface area and average pore volume increased from 474 to 870 m²/g and from 0.14 to 0.27 cc/g, respectively; whereas, for the 800 °C char the surface area and the pore volume increased from 633 to 832 m²/g and from 0.19 to 0.25 cc/g, respectively. The average pore radius however, showed no significant difference between all chars (Fig. 3, right). These results suggest that activation with CO₂ enhanced the formation of micropores, independent of the initial pyrolysis temperature. The microporous surface area of both samples was even higher than that of the commercial activated carbon (DFG 2 super) which was found to be 727 m²/g. The total surface area given by the provider was 1100 m²/g. It was therefore assumed that the commercial activated carbon had a significant amount of mesopores. The small difference in surface area between both

Table 3

Proximate and ultimate analysis of pyrolysis char samples in wt.%.

Sample	P 500	P 800	P 500 act.	P 800 act.	DFG 2 super
C	85.0	85.9	95.0	95.6	85.6
H	3.5	1.4	1.0	0.9	0.7
O	11.6	9.2	1.8	1.2	2.8
N	0.2	0.3	0.2	0.3	0.3
Volatiles	19.5	11.2	7.6	3.4	4.4
Ash	1.3	1.7	2.0	2.0	10.5

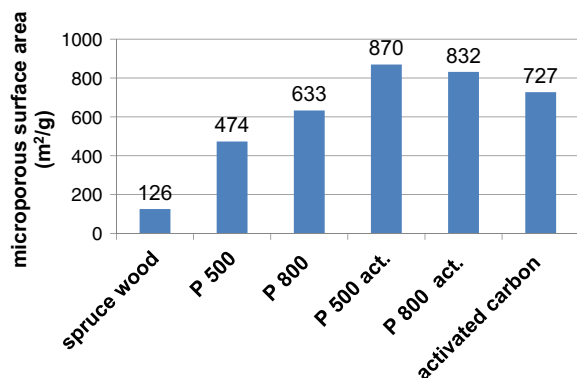


Fig. 2. Microporous surface area of spruce wood chips, char pyrolyzed at 500 and 800 °C, the respective activated samples and commercial activated carbon.

activated chars was assumed to be due to the intrinsic heterogeneity of wood char. The one-way analysis of variance (ANOVA) proved that there was no significant difference between the microporous surface area and pore volume of both activated chars (p value = 0.48), hence they were considered similar.

The surface area values for the char produced at 500 and 800 °C are consistent with the results obtained by Lopez et al. [22], who found that different wood chars produced at 600 °C had a microporous structure (pore size < 20 Å) and treatment by CO₂ at 800 °C reduced the pore sizes to below 0.8 Å. Lopez reports that the char activation with CO₂ increased the microporous surface areas from 164–390 m²/g to 557–780 m²/g, depending on the precursor wood. The measured pore volumes are also in line with available literature [28,21].

3.1.4. Surface chemistry

Fourier transform infrared spectroscopy (FTIR) was carried out for the original spruce wood and the char samples before and after activation (Fig. 4). The interpretation of the resulting spectra and the peak assignment was based on available literature [25–28,31].

The spruce wood sample showed a broad band near 3300 cm⁻¹ which was attributed to the stretching vibration of hydrogen-bonded hydroxyl groups of water. A small absorption band was observed between 2904 and 2925 cm⁻¹. This band arises usually due to aromatic CH₃, i.e. CH₃ in an aromatic ring [25] overlapping with a band due to the C–H vibration of aliphatic groups [28]. The small bands between 1587 and 1730 cm⁻¹ were attributed to the C=O stretchings for carboxyl, aldehyde, ketone and ester as well as to the aromatic ring structures [26]. The aromatic skeletal stretching bands of the spruce wood, e.g. C–O, C=C and methoxy groups of lignin, were identified in the bandwidth of 1030–1460 cm⁻¹ [26,31]. The spruce wood sample

showed a large absorption band between 848 and 1195 cm⁻¹. The maximum of this region at a bandwidth of 1030 cm⁻¹ was attributed to the symmetric C–O vibration of cellulose, hemicellulose, and lignin [26]. Additional inorganic components such as sulfates and silicates can also contribute to the broad and intensive peak at 970–1200 cm⁻¹ [26].

The spectrum of the char produced at 500 °C showed various small bands between 1560 and 1660 cm⁻¹, which were attributed to the C=C and C=O stretchings of aromatic ring structures [25] as well as to the aromatic C–H vibrations [28].

No differences could be found between the spectra of the char produced at 800 °C and the activated chars. Most of the spectral features were lost in both samples and the spectrum resembled pure graphite. This was consistent with the results found by Lopez et al. [22] and Cantrell et al. [26], who reported that secondary aromatics were fully degraded in the activated char samples along with C=O stretchings.

The O–H stretching vibration bands, usually between 3300 and 3400 cm⁻¹, were observed in none of the char samples, indicating that the oxygen in all samples was removed during pyrolysis. Sharma et al. [32] showed that the broad band for the OH in-plane bend decreased with an increase in pyrolysis temperature [31]. In contrast to the spectrum of the P 500 char, these spectra showed no peak between 1500 and 1700 cm⁻¹, indicating the absence of aromatic ring structures.

It can be concluded that the FTIR spectra of all char samples followed the trend reported by Cantrell et al. [26] for wood and biochar: (1) disappearance of lignin, cellulose and hemicellulose; (2) growth of aromatic structure at temperatures between 300 and 500 °C; and (3) decomposition and cracking of all aromatic structures at higher temperatures.

3.2. Benzene removal in a fixed bed

A fixed bed quartz reactor was used to investigate the reactivity of the different char samples for benzene removal. The results are given as the average conversion of benzene against their feeding time. The average conversion is defined by the following equation.

$$X_b = 1 - \frac{V_{b,out}}{V_{b,in}} \quad (3)$$

where $V_{b,out}$ and $V_{b,in}$ are the measured volumes of benzene coming out and going into the reactor during one measurement interval of 3 min, respectively.

3.2.1. Benzene adsorption

Adsorption of benzene on the different char samples was investigated at room temperature (23–27 °C).

Fig. 5 shows the average benzene adsorption $X_{b,ads}$ against the feeding time. At the beginning of the experiment all samples showed complete benzene adsorption ($X_{b,ads} = 1$) which decreased over time

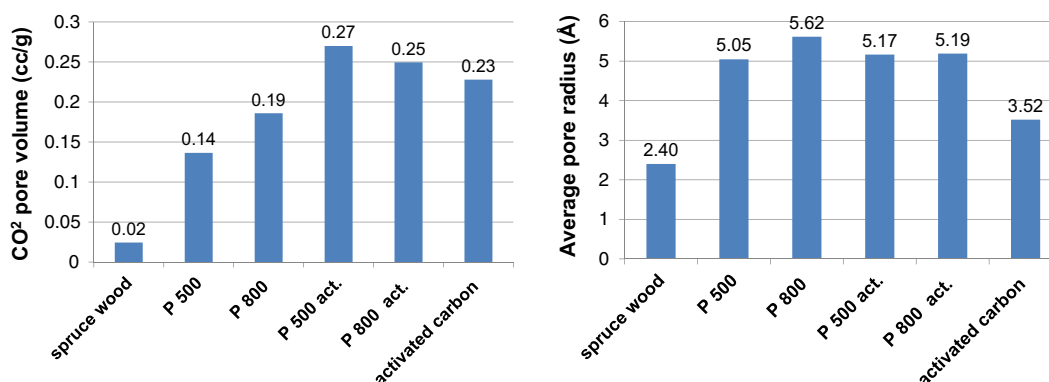


Fig. 3. DFT pore volume (left hand side) and average pore radius (right hand side) of pyrolyzed wood chips at 500 and 800 °C, and of the respective activated samples.

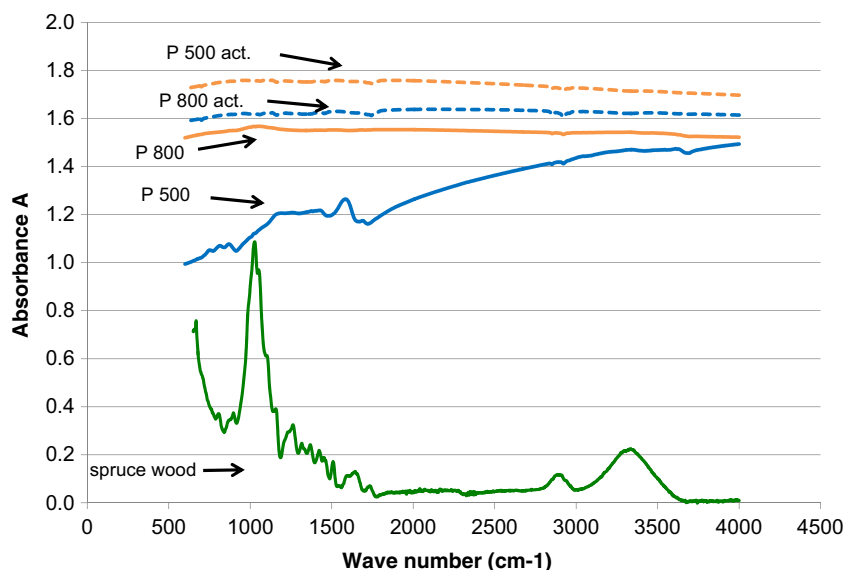


Fig. 4. FTIR spectra of the spruce wood sample of pyrolysis chars produced at 500 and 800 °C and of char activated with CO₂ at 800 °C.

indicating a deactivation of the char. While the benzene adsorption capacity of the *P 500* sample decreased rather continuously over time, the benzene adsorption capacity of the *P 800* sample decreased during the first 10 min down to $X_{b,ads} = 0.1$ and then much more slowly to $X_{b,ads} = 0.06$. Most probably, the surface area and pore volume decreased due to benzene deposition at the microporous surface. Hosokai et al. [19] found that the amount of micropores decreases to at least a half after feeding benzene with a concentration of 3 g/m³ during 30 min.

The difference between both chars can be explained by the functional groups present on the surface of the char produced at 500 °C and an increased structural ordering of the char produced at 800 °C. Moliner et al. [18] stated that the initial reaction rate of methane decomposition is related to the surface chemistry. In addition, higher pyrolysis temperatures enable a better structural ordering of the carbon matrix and a lower concentration of active sites available for reactions [33,34]. Lu et al. [13] stated that the higher structural ordering is responsible for lower char reactivity.

Another possible reason for the different benzene adsorption capacities could be the lower amount of micropores and consequently the higher amount of mesopores in *P 500* sample. Hosokai et al. [19]

found by studying the decomposition of aromatics over char that the amount of micropores decreases with increasing feeding time, while the mesopore volume remains almost constant. Hence, we conclude that benzene adsorption happens initially in the accessible micropores until they are filled and that the amount of mesopores is responsible for the long time stability of the char.

Activation with CO₂ significantly increased the benzene adsorption capacity of both char samples (p value = 0.0015). Probably, the increased adsorption capacity was due to the increase of surface area and pore volume after activation with CO₂. No difference in benzene adsorption between both activated chars was observed.

Fig. 6 plots the mass fraction of adsorbed benzene during the first 60 min compared to results with commercial activated carbon. The mass fraction of adsorbed benzene is defined as the total amount of benzene adsorbed by the char sample divided by the total amount of benzene sent into the reactor during 1 h. It was observed that the mass fraction of adsorbed benzene after passing through the *P 500* char was always higher than after passing through the *P 800* char. The one-way analysis of variance proved that the pyrolysis temperature before CO₂ activation had a significant effect (p value = 0.004) on the benzene adsorption capacity. On the other hand, the mass fraction of adsorbed benzene after passing through both activated char samples was considered to be similar (p value = 0.336). The mass fraction of adsorbed benzene was significantly higher for both activated char samples (p value = 0.0019), even higher than for the commercial activated carbon. Activation with CO₂ increased the fraction of adsorbed benzene by a factor of two or 10 for the char produced at 500 and 800 °C, respectively.

It can be concluded that the char produced at 500 °C pyrolysis temperature had a higher benzene adsorption capacity than the char produced at 800 °C and that the benzene adsorption capacity can be significantly increased by activation with CO₂.

3.2.2. Benzene cracking

Catalytic conversion of benzene over wood char was investigated at 850 °C, 950 °C, and 1050 °C at a constant benzene concentration of 4.5 g/m³ in the ingoing gas flow. The released amount of benzene and the relative char weight were recorded until the measured benzene concentration remained stable for at least 15 min. This was given after 120 min for all char samples.

Fig. 7 shows the average benzene conversion $X_{b,crack}$ at each temperature over time. The conversion measured during tests using an empty

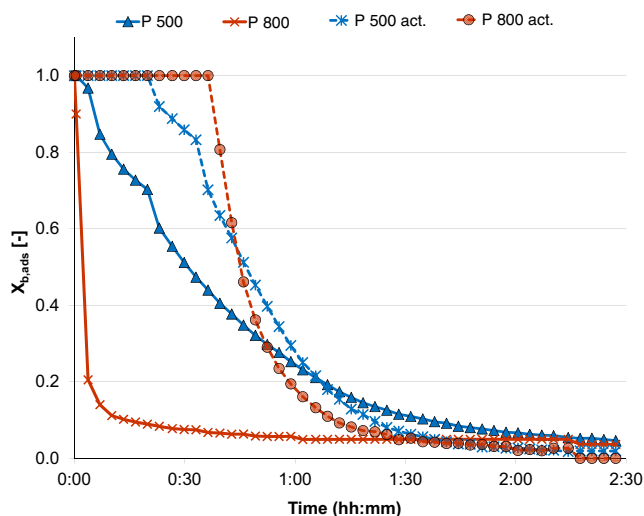


Fig. 5. Average benzene adsorption $X_{b,ads}$ over time at room temperature on char produced at 500 and 800 °C before (solid line) and after activation (dashed line).

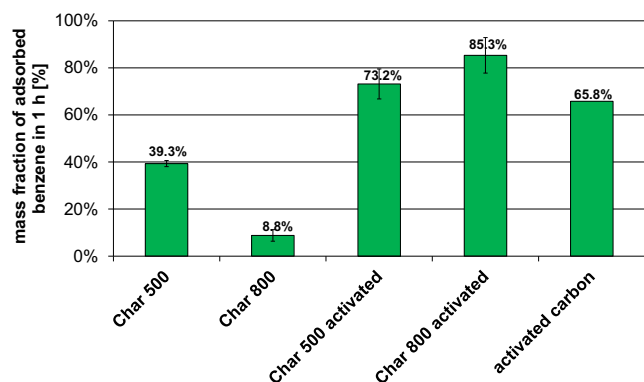


Fig. 6. Mass fraction of adsorbed benzene at the different char samples during the first 60 min compared to results with commercial activated carbon room temperature.

tube and a bed of commercial activated carbon are also included in the figure. In spite of the different internal structures, the benzene conversion of the non-activated char samples and the test without the presence of char, i.e. in an empty reactor, were very similar. A small conversion peak occurred at the first measurement of all tests indicating a 30% benzene conversion at 850 °C and 950 °C, decreasing instantaneously to a stable conversion of 3 and 20% at 850 °C and 950 °C, respectively. The small differences observed in tar conversion between the non-activated chars suggest that the surface chemistry of the char is not directly related to the char activity. Instead of the surface chemistry, other parameters such as the microporous structure may influence the char activity.

Activation with CO₂ significantly increased the benzene conversion at all temperatures. At 850 and 950 °C the activated char produced at 500 and 800 °C (*P 500 act.* and *P 800 act.*) achieved a benzene conversion of 100% at the beginning of the experiment. At both temperatures, *P 800 act.* started to deactivate after about 6 min resulting in a constant conversion of 20% after 45 min. *P 500 act.* started deactivation after about 12 min resulting in a constant conversion of about 25% after 60 min (Fig. 7(a) and (b)), indicating a higher benzene conversion activity than the *P 800 act.* char. The deactivation of the char sample is explained by coking, i.e. carbon deposition on the char surface, leading to a decrease in microporous surface area. The commercial activated carbon did not reach a complete benzene conversion at 850 °C. However, deactivation happened much slower than with the spruce char samples and conversion did not decrease below 50% during the 120 min experimental period. This was explained by a higher amount of mesopores in the activated carbon than in the activated spruce char samples. Moliner et al. [18] stated that microporous carbons exhibit high initial conversion rates but they become rapidly deactivated. In contrast, mesoporous carbons provide more stable and sustainable decomposition of light hydrocarbons [18].

Benzene conversion at 1050 °C differs from the conversion curves at lower temperatures. The activated samples achieved a complete benzene conversion during the first 12 min of the experiment, followed by a slow decrease due to deactivation of the char. In contrast to the experiment at lower temperatures, the amount of benzene converted did not decrease below 65 or 50% for *P 800 act.* or *P 500 act.*, respectively (Fig. 7(c)). This shows that at 1050 °C the char acted catalytically only during the first 30 min, and that the main mode of benzene cracking was homogeneous and hence, thermal cracking.

Fig. 8 summarizes the total amount of benzene converted during the first 60 min of the experiment. At 850 °C, benzene conversion of the char produced at 500 and 800 °C was in total lower than with the empty reactor. Most likely, when the non-activated char samples were exposed to the temperatures of pyrolysis or above, additional benzene was produced by further thermal decomposition. The maximal difference between *P 500*, *P 800* and the empty reactor as well as between

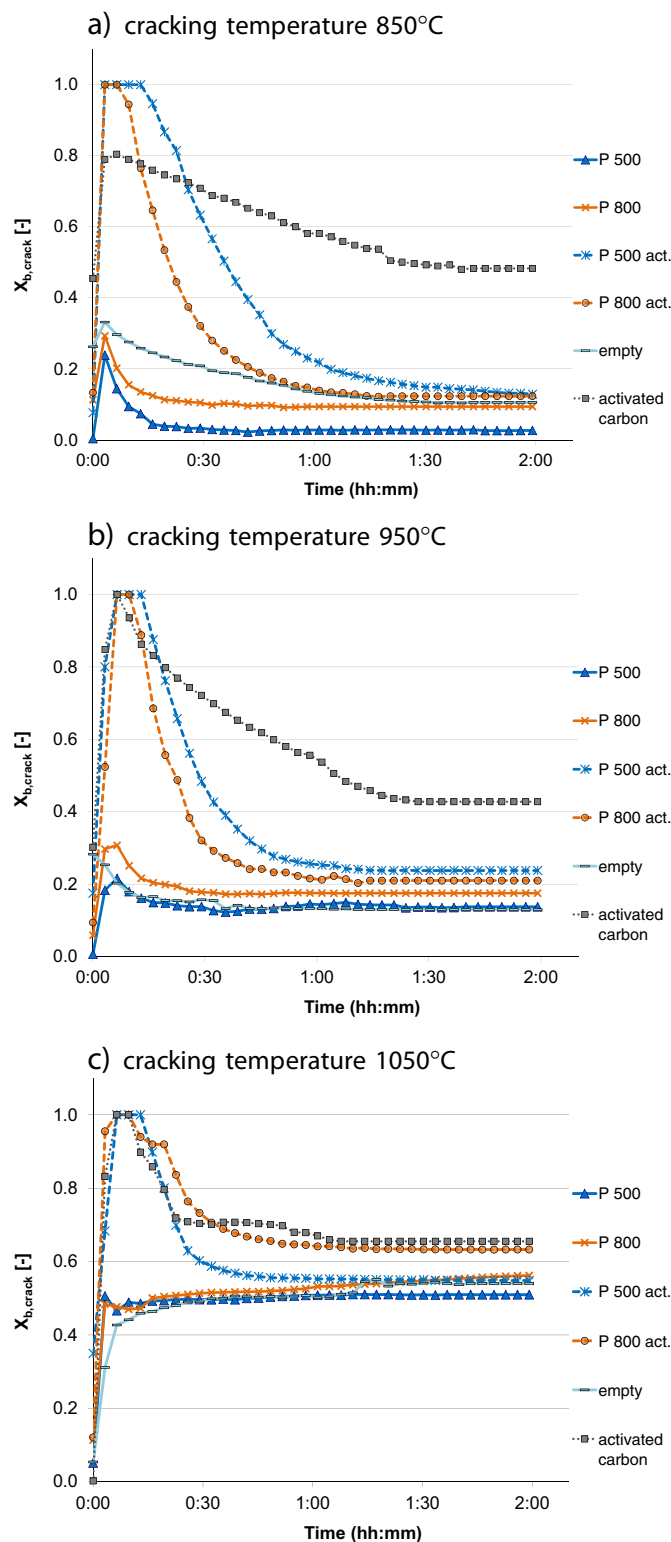


Fig. 7. Benzene conversion over char in a fixed bed at 850 °C (a), 950 °C (b) and 1050 °C (c). The solid blue and orange lines represent the char samples produced at 500 and 800 °C, respectively, while the dashed blue and orange lines the activated samples. Light blue and black dotted lines show results with an empty reactor or commercial activated carbon. Measured values are represented by symbols.

P 500 act. and *P 800 act.* was always below the difference between the activated and the non-activated samples. Therefore, it was assumed that the pyrolysis temperature had no significant effect on benzene

conversion at high temperatures. This was proven by the two-way ANOVA showing a *p* value as high as 0.457, i.e. significantly larger than the significance level 0.05. A *p*-value larger than the significance level means that the null hypothesis is proven and the difference between the measurements cannot be assumed significant [9].

Activation with CO₂ however, did significantly decrease the amount of benzene after the reactor. It was observed that at 850 and 950 °C the amount of converted benzene after reaction with the char sample *P 800 act.* was lower than that with the *P 500 act.*; on the other hand, at 1050 °C the amount of converted benzene after reaction with the char sample *P 800 act.* was higher than that with the *P 500 act.*; Some experiments showed a rather high standard deviation due to the intrinsic heterogeneity of the wood char. The one-way ANOVA indicated that the difference in benzene conversion between the char samples *P 800 act.* and *P 500 act.* was not significant (*p* value = 0.097).

We concluded that the initial pyrolysis temperature had no effect on the reactivity of the char for benzene removal and that the presence of char with a microporous surface below 700 m²/g did not improve benzene conversion at temperatures between 850 and 1050 °C. The presence of char with a microporous surface area above 800 m²/g however, does significantly reduce benzene emissions after the reactor at temperatures typical for biomass gasification processes.

The relative weight loss or gain of the different char samples after benzene cracking was analyzed in order to prove that benzene decomposes over the charcoal by coking. Fig. 9 shows the increase or decrease in weight of the char bed during the first 60 min of the experiment. According to Hosokai et al. [19], the weight balance is a measure of the extent of tar deposition on the char surface forming soot.

While the char produced at 500 and 800 °C lost weight during the benzene cracking experiment at all temperatures, the activated char samples gained weight under the same conditions. In fact, the sample weight after the experiment of the char produced at 500 and 800 °C was 88 and 90% of the initial sample weight, respectively. Most likely, the non-activated char samples underwent further outgassing due to the higher experimental temperatures, resulting in the weight loss of solid material. The weight after the experiment of the activated samples was 102 and 109% of the initial sample weight for the char produced at 500 and 800 °C, respectively. The two-way ANOVA proved a significant difference between the char samples in the relative weight loss/gain (*p* value = 1.20E−06).

The differences of the relative char weight after benzene cracking corresponded well with the different surface areas and amount of micropores in the char samples. Therefore, it was assumed that an increase of microporous surface area in the char leads to a higher benzene cracking ability since more reactive surface for the benzene

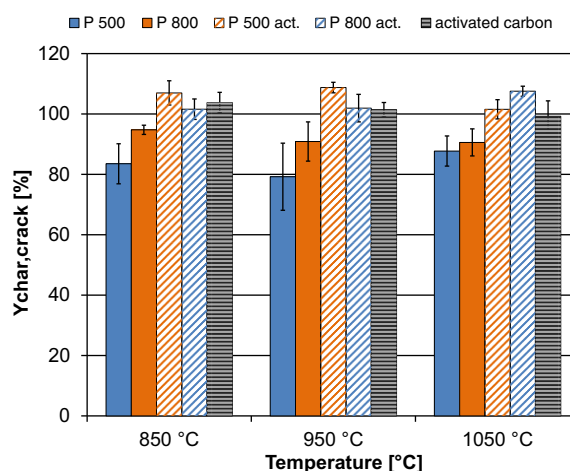


Fig. 9. Relative weight of char after benzene cracking experiments.

decomposition reaction is available. Overall, these results highlight the correlation between the weight balance and the char bed activation for benzene: the tests with a negative weight balance present a negligible benzene decomposition activity, whereas a positive weight balance indicates a catalytic effect of the char for benzene cracking.

4. Conclusion and outlook

Benzene removal over pyrolyzed spruce wood chips was investigated in a fixed bed. The produced char was analyzed in order to gain insight into its effect on benzene removal.

Analysis of the wood char showed that the microporous surface area increased with increasing pyrolysis temperature due to the formation of new micropores. Activation with CO₂ resulted in a further increase of the microporous char surface which had a remarkable impact on char reactivity for benzene removal at high temperatures. The total microporous surface area above 700 m²/g was found to be a good indicator for the reactive surface of the char at temperatures between 850 and 1050 °C. At 1050 °C, the main mode of benzene conversion was found to be homogeneous thermal decomposition. The differences of the relative char weight after benzene cracking corresponded well with the different amounts of micropores in the char samples: the tests with a negative weight balance presented a negligible benzene conversion activity, whereas a positive weight balance indicated a catalytic effect of the char for benzene cracking.

In practical biomass gasification with air or oxygen as gasification agent the concentration of CO₂ in the hot product gas is at least 10–20 vol.%. In processes with a bed of charcoal, CO₂ gasification of charcoal would occur simultaneously with decomposition of benzene by coking over charcoal surface. Coke deposition from benzene would influence the charcoal gasification while the gasification would form micropores as active sites for coking in/on the charcoal. It is hence worth to investigate in future studies benzene decomposition both in the presence and absence of CO₂ for char activation.

It should be noted that the experimental conditions adopted in this study are similar to those applied in conventional fixed-bed reactors and the results can be directly applied to that technology only. In other pyrolysis and gasification processes (for example where high heating rates are applied), different results could be obtained and further research is required.

Acknowledgment

The authors are grateful to all colleagues and students for their help and support, and in particular to Dr. Alexander Susdorf for his advice during the lab work at Fraunhofer ISE. Philipp Hügenell is gratefully

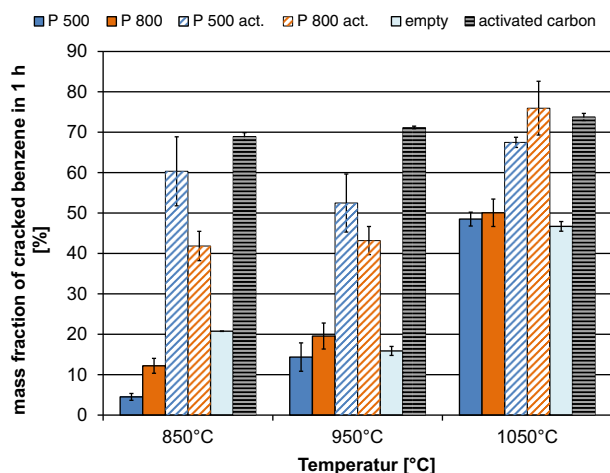


Fig. 8. Mass fraction of decomposed benzene at 850 °C, 950 °C and 1050 °C during the first 60 min of the cracking experiment.

acknowledged, whose cooperation was very helpful to carry out surface and pore size measurements in the lab facilities of the Department Thermal Systems and Buildings of the Fraunhofer ISE.

References

- [1] C. Li, K. Suzuki, Tar property, analysis, reforming mechanism and model for biomass gasification — an overview, *Renewable and Sustainable Energy Reviews* 13 (2009) 594–604.
- [2] L. Burhenne, L. Rochlitz, C. Lintner, T. Aicher, Technical demonstration of the novel Fraunhofer ISE biomass gasification process for the production of a tar-free synthesis gas, *Fuel Processing Technology* 106 (2013) 751–760.
- [3] K. Maniatis, A. Beenackers, Tar protocols. IEA bioenergy gasification task, *Biomass and Bioenergy* 18 (2000) 1–4.
- [4] S. Anis, Z. Zainal, Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods — a review, *Renewable and Sustainable Energy Reviews* 15 (2011) 2355–2377.
- [5] Z.A. El-Rub, E. Bramer, G. Brem, Experimental comparison of biomass chars with other catalysts for tar reduction, *Fuel* 87 (2008) 2243–2252.
- [6] T. Phuphuakrat, T. Namioka, K. Yoshikawa, Tar removal from biomass pyrolysis gas in two-step function of decomposition and adsorption, *Applied Energy* 87 (2010) 2203–2211.
- [7] Q. Sun, S. Yu, F. Wang, J. Wang, Decomposition and gasification of pyrolysis volatiles from pine wood through a bed of hot char, *Fuel* 90 (2011) 1041–1048.
- [8] C.D. Blasi, Combustion and gasification rates of lignocellulosic chars, *Progress in Energy and Combustion Science* 35 (2009) 121–140.
- [9] L. Burhenne, M. Damiani, T. Aicher, Effect of feedstock water content and pyrolysis temperature on the structure and reactivity of spruce wood char produced in fixed bed pyrolysis, *Fuel* 107 (2013) 836–847.
- [10] P. Gilbert, C. Ryu, V. Sharifi, J. Swithenbank, Tar reduction in pyrolysis vapours from biomass over a hot char bed, *Bioresource Technology* 100 (2009) 6045–6051.
- [11] D. Fuentes-Cano, A. Gomez-Barea, S. Nilsson, P. Ollero, Decomposition kinetics of model tar compounds over chars with different internal structure to model hot tar removal in biomass gasification, *Chemical Engineering Journal* 228 (2013) 1223–1233.
- [12] M.J. Antal, M. Groenli, The art, science, and technology of charcoal production, *Industrial & Engineering Chemistry Research* 42 (2003) 1619–1640.
- [13] L. Lu, C. Kong, V. Sahajwalla, D. Harris, Char structural ordering during pyrolysis and combustion and its influence on char reactivity, *Fuel* 81 (2002) 1215–1225.
- [14] M. Asadullah, S. Zhang, C.-Z. Li, Evaluation of structural features of chars from pyrolysis of biomass of different particle sizes, *Fuel Processing Technology* 91 (2010) 877–881.
- [15] C. Myren, C. Hoernell, E. Bjoernbom, K. Sjoestroem, Catalytic tar decomposition of biomass pyrolysis gas with a combination of dolomite and silica, *Biomass and Bioenergy* 23 (2002) 217–227.
- [16] J. Fjellerup, J. Ahrenfeldt, U. Henriksen, B. Gøbel, Formation, Decomposition and Cracking of Biomass Tars in Gasification, Department of Mechanical Engineering, 2005.
- [17] M.L. Boroson, J.B. Howard, J.P. Longwell, W.A. Peters, Heterogeneous cracking of wood pyrolysis tars over fresh wood char surfaces, *Energy & Fuels* 3 (1989) 735–740.
- [18] R. Moliner, I. Suelves, M. Lazaro, O. Moreno, Thermocatalytic decomposition of methane over activated carbons: influence of textural properties and surface chemistry, *International Journal of Hydrogen Energy* 30 (2005) 293–300.
- [19] S. Hosokai, K. Kumabe, M. Ohshita, K. Norinaga, C.-Z. Li, J. Hayashi, Mechanism of decomposition of aromatics over charcoal and necessary condition for maintaining its activity, *Fuel* 87 (2008) 2914–2922.
- [20] B. Feng, S.K. Bhatia, Variation of the pore structure of coal chars during gasification, *Carbon* 41 (2003) 507–523.
- [21] A.R. Sanchez, A.A. Elguzabal, L. de La Torre Saenz, CO₂ activation of char from *Quercus agrifolia* wood waste, *Carbon* 39 (2001) 1367–1377.
- [22] F.A. Lopez, T.A. Centeno, I. Garcia-Diaz, F.J. Alguacil, Textural and fuel characteristics of the chars produced by the pyrolysis of waste wood, and the properties of activated carbons prepared from them, *Journal of Analytical and Applied Pyrolysis* 104 (2013) 551–558.
- [23] S. Guo, J. Peng, W. Li, K. Yang, L. Zhang, S. Zhang, H. Xia, Effects of CO₂ activation on porous structures of coconut shell-based activated carbons, *Applied Surface Science* 255 (2009) 8443–8449.
- [24] T. Zhang, W.P. Walawender, L. Fan, M. Fan, D. Dugaard, R. Brown, Preparation of activated carbon from forest and agricultural residues through CO₂ activation, *Chemical Engineering Journal* 105 (2004) 53–59.
- [25] R. Sharma, J. Wooten, V. Baliga, M. Hajaligol, Characterization of chars from biomass-derived materials: pectin chars, *Fuel* 80 (2001) 1825–1836.
- [26] K.B. Cantrell, P.G. Hunt, M. Uchimiya, J.M. Novak, K.S. Ro, Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar, *Bioresource Technology* 107 (2012) 419–428.
- [27] D.M. Keown, J.-I. Hayashi, C.-Z. Li, Drastic changes in biomass char structure and reactivity upon contact with steam, *Fuel* 87 (2008) 1127–1132.
- [28] S. Gaspard, S. Altenor, E. Dawson, P. Barnes, A. Ouensanga, Activated carbon from vetiver roots: gas and liquid adsorption studies, *Journal of Hazardous Materials* 144 (2007) 73–81.
- [29] H. Darmstadt, D. Pantea, L. Suemmenchen, U. Roland, S. Kaliaguine, C. Roy, Surface and bulk chemistry of charcoal obtained by vacuum pyrolysis of bark: influence of feedstock moisture content, *Journal of Analytical and Applied Pyrolysis* 53 (2000) 1–17.
- [30] K.A. Davis, R.H. Hurt, N.Y. Yang, T.J. Headley, Evolution of char chemistry, crystallinity, and ultrafine structure during pulverized-coal combustion, *Combustion and Flame* 100 (1995) 31–40.
- [31] E. Apaydin-Varol, A.E. Putun, Preparation and characterization of pyrolytic chars from different biomass samples, *Journal of Analytical and Applied Pyrolysis* 98 (2012) 29–36.
- [32] R.K. Sharma, J.B. Wooten, V.L. Baliga, X. Lin, W.G. Chan, M.R. Hajaligol, Characterization of chars from pyrolysis of lignin, *Fuel* 83 (2004) 1469–1482.
- [33] C.D. Blasi, C. Branca, S. Sparano, B.L. Mantia, Drying characteristics of wood cylinders for conditions pertinent to fixed-bed countercurrent gasification, *Biomass and Bioenergy* 25 (2003) 45–58.
- [34] F. Mermoud, F. Golfier, S. Salvador, L.V. de Steene, J. Dirion, Experimental and numerical study of steam gasification of a single charcoal particle, *Combustion and Flame* 145 (2006) 59–79.